

# First-principles studies of the Optical anisotropy of $R3(\text{No.146})$ space group chalcogenides crystal $\text{AX}_2\text{MQ}_6$

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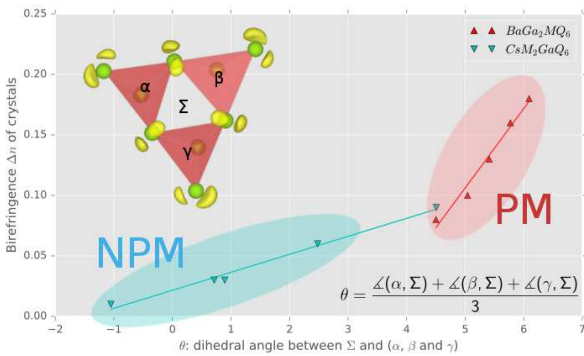
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## Abstract

The birefringence values of  $R3(\text{No.146})$  space group crystals  $\text{AX}_2\text{MQ}_6$  have been calculated. Their Electron Localization Function(ELF) was calculated to show that the acentricity of the bonds on  $sp^3$  hybridization  $Q^{2-}$  ions is the main origin of optical anisotropy. To quantificat the acentricity, a geometric parameter dihedral angle between tetrahedral undersides and  $xy$ -planes was defined. We find theoretically the birefringence depend on the defined geometric parameter and ion radius. This relation between birefringence and structure can be used to explain the abnormal difference of birefringence of isostructural  $\text{AX}_2\text{MQ}_6$  and  $\text{AX}_4\text{M}_5\text{Q}_{12}$  and useful for exploring new phase matching IR-NLO crystal.

## I. TOC

## II. INTRODUCTION



IR-NLO materials contain the following conditions will have potential applicability:

- Large second nonlinear optical susceptibility  $\chi$  for a IR-NLO crystal which should be at least 10 times (preferably 20 times) larger than that of KDP ( $d_{max} = 0.39 \text{ pm}$ ).<sup>1</sup>
- An moderate birefringence and linear optical dispersion which make the crystal phase-matched in the condition is necessary.<sup>2</sup> The appropriate birefringence should be large enough to achieve the phase-matching in the IR region but not too large to generate considerable self-focus<sup>3</sup> and walk-off effects<sup>4</sup>.
- Large band gap  $E_g$  for high laser damage threshold<sup>5</sup>.

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The  $AX_4M_5Q_{12}$ <sup>6</sup> synthesised by H Lin *et al.* have strong NLO response (roughly 16-40 times that of commercial  $AgGaS_2$ ) at IR range. However, the birefringence of these compounds come near to zero which means they are close to isotropic crystal which are impossible to reach type I phase matching. On the contrary, the  $BaGa_2SnSe_6$ <sup>7</sup> synthesised by X Li *et al.* have extremely large birefringence values and exhibits very strong NLO response( 5.2 times that of the benchmark  $AgGaS_2$  at the laser frequency 2.09  $\mu m$ ). There are some symmorphic structures  $BaGa_2MQ_6$ <sup>8</sup> ( $M = Si, Ge$ ;  $Q = S, Se$ ) published by W Yin *et al.* and  $CsSn_2XSe_6$  ( $X = In, Ga$ ) published by H Lin *et al.* exhibits moderate birefringence and large bandgaps.

The  $AX_2MQ_6$  and  $AX_4M_5Q_{12}$  have the similar structure which belongs to  $R3(No.146)$  space group and can be derived from the zinc-blende structure so that we call them the diamond-like framework structure(DLF)<sup>9</sup>. The two similar structure show the entirely different anisotropic properties. The birefringence value of  $AX_4M_5Q_{12}$  is very small ( $<0.01$ ) while  $AX_2MQ_6$  have a wide range birefringence (0.006 to 0.186) in transmission wavelengths<sup>6</sup>.

In transparent materials, refractive index is proportional to the square root of the electronic polarization. The latter is in turn proportional to the polarizabilities of the ions in the crystal and also the local electric field.<sup>10</sup> And optical anisotropy gives rise to the phenomenon of birefringence.<sup>11</sup> We can calculate the values of refractive index by using ab initio and empirical (or semiempirical) methods<sup>12,13</sup>. The ab initio method is difficult to construct explicit structural-properties relation though it can be taken to make precise values of refractive index. As for empirical(or semiempirical) methods, they only calculated the mean refractive indices without consideration of birefringence.

The refractive indices of materials strongly relate to the space structure. Densely packed arrays of highly polarizable groups result in large refractive indices. And the different direction of polarizable groups lead to the different refractive indices of ordinary and extraordinary optical planes which is the reason of birefringence of crystals<sup>10</sup>. The structural-birefringence relationship is revealed in some 0D inorganic borate materials<sup>14,15</sup>. These borate materials are constructed by isolated B—O groups which is the dominating factors of anisotropy so that the packed mode can be easily described to relate birefringence. However,  $AX_2MQ_6$  and  $AX_4M_5Q_{12}$  are 3D inorganic crystals which are hard to attribute the optical

anisotropy to isolate groups or molecules.

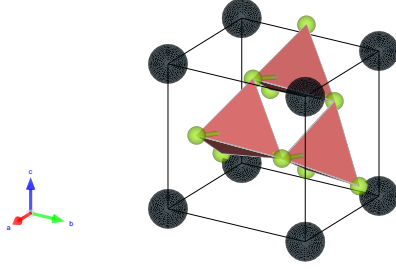
In our work, we develop a reasonable way to deal with site partial occupation in these structure. Then conclude  $CsSn_2GaSe$  and five existent  $BaGa_2XQ_6$  compounds which have different birefringence and nonlinear optical susceptibility to reveal the dependence on the ion radius and the defined geometric parameters of birefringence. Derived from these six isosymorphic compounds, we construct four hypothetical compounds  $CsM_2GaQ_6$  ( $M=Si,Ge$ ;  $Q=S,Se$ ) to confirm the defined geometric parameters dependence. The Electron Localization Function(ELF)<sup>16</sup> was represented to explain the reason why we defined the dihedral angle between tetrahedral undersides and xy-planes and show the relation of structure and optical anisotropy.

### III. COMPUTATIONAL METHOD

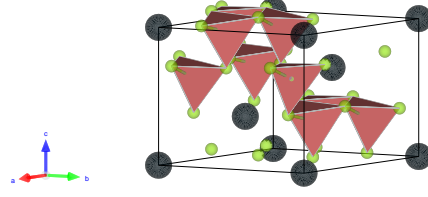
To deal with the fractional site occupation uncertainty in  $AX_2MQ_6$ , the twelve initial geometries of structures represented in a hexagonal conventional cell was enumerated by using SOD(site-occupancy disorder) program<sup>17</sup>. The DFT and optical property calculations in the study were performed using the Quantum-Espresso(QE)<sup>18</sup> and Vienna Ab initio Simulation Package (VASP)<sup>19</sup>.

Geometries relaxation were performed in QE optimized using PBEsol<sup>20</sup> GGA with pz-LDA and PBE as comparison. Electronic wave functions (density) were expanded in plane waves up to 40Ry (320Ry) and ultrasoft pseudopotential (rrkjus) was used to treat valence electrons. Pseudovalence electronic configurations were Cs:  $6s^1$ , Ba:  $5s^25p^65s^2$ , Cd:  $4d^95s^25p^{0.5}$ , Ga:  $3d^{10}4s^24p^1$ , In:  $4d^{10}5s^25p^1$ , Sn:  $4d^{10}5s^25p^2$ , Si:  $3s^23p^23d^{-2}4f^{-2}$ , Ge:  $3d^{10}4s^24p^2$ , Se:  $3d^{10}4s^24p^44d^{-2}$  and S:  $3s^23p^43d^{-2}$ . Monkhorst-Pack (MP)<sup>21</sup> k-point meshes were used for the Brillouin zone (BZ) integrations and convergence was tested to zone-edge-shifted  $4 \times 4 \times 4$ . During structure relaxation, the forces were converged to values of less than 0.001 a.u.

In the linear optical properties calculation done with VASP, a projector-augmented plane-wave method<sup>22</sup>, with 600-eV energy cutoff was utilized and with the electronic configuration for the involved elements: Cs:  $5s^25p^66s^1$ , Ba:  $5s^25p^66s^2$ , Cd:  $5s^24d^{10}$ , Ga:  $4s^24p^1$ , In:  $5s^25p^1$ , Sn:  $5s^25p^2$ , Si:  $3s^23p^2$ , Ge:  $3d^{10}4s^24p^2$ , Se:  $4s^24p^4$  S:  $3s^23p^4$ . To get reasonable optical properties, brillouin zone sampling meshes were increased and tested to convergence to  $9 \times 9 \times 9$  with none-shifted Monkhorst-Pack (MP) method.



(a) Rhombohedral setting



(b) Hexagonal setting

**Figure 1** Two settings for  $AX_2MQ_6$  crystals

VASP calculates the frequency dependent dielectric matrix after the electronic ground state has been determined. The imaginary part is determined by a summation over empty states using the equation<sup>23</sup>:

$$\varepsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi^2 e^2}{\Omega} \times \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(\varepsilon_c k - \varepsilon_v k - \omega) \times \langle u_{ck+e_{aq}} | u_{vk} \rangle \langle u_{ck+e_{aq}} | u_{vk} \rangle^* \quad (1)$$

where the indices  $c$  and  $v$  refer to conduction and valence band states respectively, and  $u_{ck}$  is the cell periodic part of the orbitals at the  $k$ -point  $k$ . This method is performed without containing the local-Field effects<sup>24</sup> and excitonic effects<sup>25</sup>.

The real part of the dielectric tensor  $\varepsilon^{(1)}$  is obtained by the usual Kramers-Kronig transformation

$$\varepsilon_{\alpha\beta}^{(1)}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_{\alpha\beta}^{(2)}(\omega') \omega'}{\omega'^2 - \omega^2 + i\eta} d\omega' \quad (2)$$

where  $P$  denotes the principle value.

The static second-order susceptibility,  $\chi^{(2)}$ , is important for characterizing the NLO properties. The crystal orbital or band structure methods to calculate the NLO coefficients have been greatly improved and successfully used to predict the SHG coefficients for semiconductors and insulators. The length-gauge formalism derived by Aversa and Sipe<sup>26</sup> and modified by Rashkeev *et al.*<sup>27</sup> is adopted in our calculation. The imaginary part of the static second-order optical susceptibility can be ex-

pressed as:

$$\begin{aligned} \chi^{abc} &= \chi_e^{abc} + \chi_i^{abc} \\ &= \frac{e^3}{\hbar\Omega} \sum_{nml,k} \frac{r_{nm}^a \{r_{ml}^b r_{ln}^c\}}{\omega_{nm}\omega_{ml}\omega_{ln}} [\omega_n f_{ml} + \omega_m f_{ln} + \omega_l f_{nm}] \\ &\quad + \frac{i}{4} \frac{e^3}{\hbar\Omega} \sum_{nm,k} \frac{f_{nm}}{\omega_{mn}^2} [r_{nm}^a (r_{mn;c}^b + r_{mn;b}^c) \\ &\quad + r_{nm}^b (r_{mn;c}^a + r_{mn;a}^c) + r_{nm}^c (r_{mn;b}^a + r_{mn;a}^b)]. \end{aligned} \quad (3)$$

## IV. RESULTS AND DISCUSSION

### i. Structure and Electronic Structure

The  $AX_2MQ_6$  belong to trigonal crystal system and have R3(No.146) space group symmetry with  $A=\text{Cs, Ba}$ ;  $Q=\text{S, Se}$ . To balance the valence,  $X$  and  $M$  are 3+ and 4+ respectively for  $A=\text{Ba}$  or  $X=X^{4+}$  and  $M=M^{3+}$  if  $A=\text{Cs}$ . There are two ways to represent R3 space group crystal, in hexagonal setting Fig.1b or Rhombohedral setting 1a.<sup>28</sup>

Taking  $\text{BaX}_2\text{MQ}_6$  as object of study and representing by using rhombohedral setting, the unit cell contains 10 atoms that Ba ion on vertex and three  $[(X/M)Q_4]^{n-}$  tetrahedral anions. Fig.1a The structural analysis reveals that  $X$  and  $M$  randomly occupy the same Wyckoff site 3b with the ratio of  $X:M=2:1$ <sup>8</sup>. Viewed from the screw  $3_1$ -axis, xy-planes are tiled by the bundles of three tetrahedrons shown in Fig.???. This kind of relatively dispersive occupation of tetrahedral bundles potentially influence the freedom of tetrahedral polarizable directions which lead to the different birefringence of  $AX_2MQ_6$  as we will discuss later.

In order to proper deal with the DFT calculation, we are going to choose one complete occupation configuration by using SOD program. Instead of extending

|                                     |             |            |           |
|-------------------------------------|-------------|------------|-----------|
| BaGa <sub>2</sub> SiSe <sub>6</sub> | a           | c          | V         |
| exp                                 | 9.5544(2)   | 8.6498(4)  | 683.82(2) |
| PBEsol                              | 9.462       | 8.556      | 663.318   |
| BaGa <sub>2</sub> SiSe <sub>6</sub> | a           | c          | V         |
| exp                                 | 9.967(1)    | 9.047(2)   | 778.3(2)  |
| PBEsol                              | 9.925       | 9.006      | 768.225   |
| BaGa <sub>2</sub> GeSe <sub>6</sub> | a           | c          | V         |
| exp                                 | 9.6020(1)   | 8.6889(2)  | 693.78(2) |
| PBEsol                              | 9.502       | 8.623      | 674.275   |
| BaGa <sub>2</sub> GeSe <sub>6</sub> | a           | c          | V         |
| exp                                 | 10.008(1)   | 9.090(2)   | 788.4(2)  |
| PBEsol                              | 9.949       | 9.093      | 779.410   |
| BaGa <sub>2</sub> SnSe <sub>6</sub> | a           | c          | V         |
| exp                                 | 10.1449(14) | 9.2490(18) | 824.4     |
| PBEsol                              | 10.054      | 9.326      | 816.477   |

**Table 1** Lattice parameters compare with experiment data

the rhombohedral primitive cell to supercell and collect different models, we adopt hexagonal axes representation which is three times larger in cell volume of the rhombohedral primitive cell. Consequently, we enumerate all twelve nonequivalent configurations from a 1x1x1 hexagonal primitive cell as list in SI fig\*. After analyse symmetry of twelve configurations, we get nine  $P1$ (No.1) space group configurations and three configurations whose space group are  $P3_2$ (No.145),  $P3_1$ (No.144) and  $P3$ (No.143) respectively which are subgroups of  $R3$ (No.146). To conform with the X-ray diffraction experiment results that the lattice parameters  $a$  and  $b$  in the conventional cell are equal, we excluded nine  $P1$  configurations and compare the ground state energy of the relaxed  $P3$ ,  $P3_1$ ,  $P3_2$  configurations to choose the most resonable object for the subsequent study.

Three configurations  $P3_2$ (No.145),  $P3_1$ (No.144) and  $P3$ (No.143) of each BaGa<sub>2</sub>MQ<sub>6</sub> compound is relax to optimal structure and then the groud state energy is extracted. Three kinds of DFT exchange-correlate energy are employed: (1) using LDA (2) using PBE and (3) using PBEsol. Results are summarised in Table.4. It shows PBEsol can precively describe the ground state structure of BaGa<sub>2</sub>MQ<sub>6</sub>. From Table.5 we can find that  $P3_2$  and  $P3_1$  configurations always have lower energy than  $P3$  configurations, which means the model of these two configurations are more closely similar to the real crystal structures.

We conclude from the data that the more dispersive the occupied atom species are, the lower the groud state energy are. The  $P3_1$ (No.144) model relaxed by using PBEsol is suitable as the object to continue the properties

calculation. Therefore we take the  $P3_1$ (No.144) configuration with PBEsol relaxed structure as the model for subsequent property studies.

The band structures are shown in Fig[] in the Supporting Information. From the band structure, we find all AX<sub>2</sub>MQ<sub>6</sub> are indirect band crystal with calculated band gap range from 1.332eV to 3.078eV for CsGa<sub>2</sub>SnSe<sub>6</sub> to CsSi<sub>2</sub>GaSe<sub>6</sub>. The values of band gap are decrease with the atomic number. Analysis of the partail density of states (PDOS) (Table.??) show that A<sup>n+</sup> cations mainly occupied the energy far below the fermi energy. The transition from occupied states to unoccupied states are mainly determinated by Q<sup>2-</sup> atoms. And this is the reason of subsequent analysis of birefringence that we focus on the acentricity of the sp<sup>3</sup> hybridization Q<sup>2-</sup> ions.

## ii. Stability of hypothetical CsGaM<sub>2</sub>Q<sub>6</sub>

Up to now, five kinds of BaGa<sub>2</sub>MQ<sub>6</sub> with M=Si,Ge,Sn; Q=S,Se, CsGaSn<sub>2</sub>Se and CsInSn<sub>2</sub>Se have been synthesized, which can be taken as indication of the stabilities of the derived hypothetical crystals CsGaM<sub>2</sub>Q<sub>6</sub> with M=Si,Ge and Q=S,Se. We calculated the cohesive energies of AX<sub>2</sub>MQ<sub>6</sub>, which is defined as the energy required to form separated neutral atoms in their ground electronic state from the state at 0K and 1atm.[] Cohesive energies of AX<sub>2</sub>MQ<sub>6</sub> are obtained using the expression:

$$E_C = \{ \sum_n p_n E_c[n] - E_t[Crystal] \} / \sum p_n \quad (4)$$

$n$  is the atom species of crystal.

The calculated cohesive energies of seven existent structure and four deuterogenic structure CsM<sub>2</sub>GaQ<sub>6</sub> are given in Table.2. We note that even CsM<sub>2</sub>GaQ<sub>6</sub> (M=Si,Ge; Q= S, Se) are not synthesised yet, they are more cohesive energy stable.

## iii. Linear Optical properties of AX<sub>2</sub>MQ<sub>6</sub> crystals

The model we adopt to calculate the optical properties are the  $R3$  (No.144) space group configuration and its point group is  $C_3$  which belongs to the uniaxial crystal classes. Therefore only two independent dielectric constant  $\epsilon_{xy}$ (in plane component the average over the x and the y directions) and  $\epsilon_z$ (z component perpendicular to  $\epsilon_{xy}$ ) will appear in the results.

In synthetic chemistry, phase matching ability is tested by using the Kurtz-Perry powder<sup>29</sup> method (without

**Table 2** Cohesive energies  $E_C$  of  $AGa_2QM_6$  crystals.

| Structure                           | $E_C \times \sum p_n (\text{eV})$ | Structure                           | $E_C (\text{eV})$ |
|-------------------------------------|-----------------------------------|-------------------------------------|-------------------|
| BaGa <sub>2</sub> SiS <sub>6</sub>  | 119.923                           | CsSi <sub>2</sub> GaS <sub>6</sub>  | 116.981           |
| BaGa <sub>2</sub> SiSe <sub>6</sub> | 107.812                           | CsSi <sub>2</sub> GaSe <sub>6</sub> | 104.288           |
| BaGa <sub>2</sub> GeS <sub>6</sub>  | 114.790                           | CsGe <sub>2</sub> GaS <sub>6</sub>  | 106.897           |
| BaGa <sub>2</sub> GeSe <sub>6</sub> | 103.834                           | CsGe <sub>2</sub> GaSe <sub>6</sub> | 96.689            |
| BaGa <sub>2</sub> SnSe <sub>6</sub> | 102.515                           | CsSn <sub>2</sub> GaSe <sub>6</sub> | 94.356            |

needs of single crystals). These are type-I phase matching case in which the two lower-frequency waves have the same polarization<sup>30,4</sup>.

In positive uniaxial crystal and for the type I phase matching the condition is:

$$\begin{aligned} n_e^v &> n_o^{2v} \quad \text{or} \\ n_e^{2v} - n_o^{2v} &> n_e^{2v} - n_o^v \end{aligned} \quad (5)$$

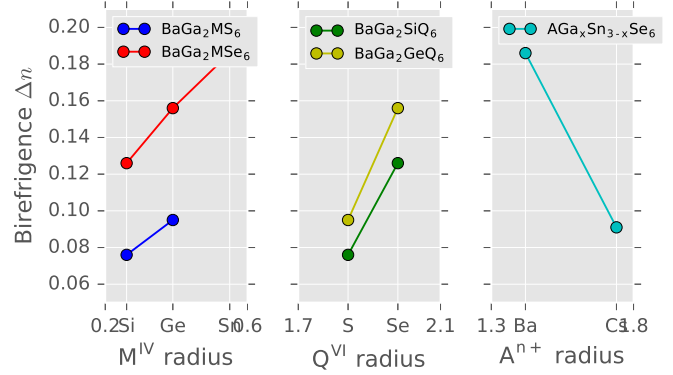
which is different from the type I negative uniaxial crystal phase matching condition:

$$\begin{aligned} n_o^v &> n_e^{2v} \quad \text{or} \\ n_o^{2v} - n_e^{2v} &> n_o^{2v} - n_o^v \end{aligned} \quad (6)$$

Both expressions 5 and 6 for negative and positive uniaxial crystals show that if birefringence in frequency  $2\nu$  is larger, the phase matching condition is more possible to be achieved (exceptional case may result from intensity depend index of refractive<sup>31</sup> or abnormal dispersion behaviour<sup>14</sup>). This is how we related the phase matching ability with the birefringence, although the refractive index of many optical materials depends on the intensity of the light when using the high energy light.

The calculated imaginary parts of the dielectric function for the  $AX_2MQ_6$  crystals for photon energy up to 10eV are shown in SI. The refractive index are calculated and then resolved into two components, the in-plane component  $n_{xy}$  i.e. ordinary refractive index  $n_o$  is the average over the x and the y directions and the z component i.e. extraordinary refractive index which is perpendicular to  $n_{xy}$ . To relate the phase matching abilities with linear optical properties, we calculated  $\Delta n_{2\nu}, \Delta n_o$  and  $n_e^v - n_o^{2v}$  and put them in Table.3.

Calculation of the birefringence in  $AX_2MQ_6$  structures reveal the following regularities: The birefringence value increase with increasing ion radius. We use the Pauling ion radius<sup>32</sup>. If the change of the absolute value of  $\Delta n_o$  is considered, it is seen from Fig.2 that in substituting for the filling cations (Ba  $\rightarrow$  Cs) or for the framework (Si

**Figure 2** The dependence of the birefringence of  $AX_2MQ_6$  crystals on the Pauling ion radii R

$\rightarrow$  Ge  $\rightarrow$  Sn), (S  $\rightarrow$  Se) anions in  $AX_2MQ_6$  compounds, the birefringence value is positively correlated with ion radius.

#### iv. Distinct anisotropy of $AX_2MQ_6$ and $AX_4M_5Q_{12}$

In transparent materials, refractive index is proportional to the square root of the electronic polarization. The latter is in turn proportional to the polarizabilities of the ions in the crystal and also the local electric field. Densely packed arrays of highly polarizable group alignment result in large refractive indices. The different direction of anisotropic groups lead to the different refractive indices of ordinary and extraordinary optical planes which is the reason of birefringence of crystals.

Both  $AX_2MQ_6$  and  $AX_4M_5Q_{12}$  belong to space group R3(No.146) and can be derived from zinc-blende structure that is why we call these structures diamond-like framework (DLF) structure. From the angle of view perpendicular to c axis (the  $C_3$  rotation axis), the crystal can be cut to layers constructed by polarized tetrahedrons. The layers viewed from c axis (Fig.3a, Fig.3c) are different for  $AX_2MQ_6$  and  $AX_4M_5Q_{12}$  but both can be regarded as

**Table 3** Structure and optical properties of  $AX_2MQ_6$  crystals.

| Compounds                           | dihedral angle $\theta$ | $\Delta n^0$ | $\Delta n^{2v}$ | $ \chi_{max}^{(2)} $ | $n_e^v - n_o^{2v}$ | band gap (eV) |
|-------------------------------------|-------------------------|--------------|-----------------|----------------------|--------------------|---------------|
| BaGa <sub>2</sub> SiS <sub>6</sub>  | 4.501                   | 0.076        | 0.083           | 39.382               | +                  | 2.823         |
| BaGa <sub>2</sub> SiSe <sub>6</sub> | 5.410                   | 0.126        | 0.143           | 76.014               | +                  | 2.166         |
| BaGa <sub>2</sub> GeS <sub>6</sub>  | 5.041                   | 0.095        | 0.106           | 45.417               | +                  | 2.358         |
| BaGa <sub>2</sub> GeSe <sub>6</sub> | 5.771                   | 0.156        | 0.197           | 102.139              | +                  | 1.507         |
| BaGa <sub>2</sub> SnSe <sub>6</sub> | 6.091                   | 0.186        | 0.269           | 159.946              | +                  | 1.412         |
| CsSi <sub>2</sub> GaS <sub>6</sub>  | -1.05                   | 0.006        | 0.008           | 38.518               | -                  | 3.078         |
| CsSi <sub>2</sub> GaSe <sub>6</sub> | 0.892                   | 0.025        | 0.029           | 67.926               | -                  | 2.351         |
| CsGe <sub>2</sub> GaS <sub>6</sub>  | 0.713                   | 0.027        | 0.033           | 51.340               | -                  | 2.536         |
| CsGe <sub>2</sub> GaSe <sub>6</sub> | 2.480                   | 0.061        | 0.085           | 110.475              | -                  | 1.648         |
| CsSn <sub>2</sub> GaSe <sub>6</sub> | 4.507                   | 0.091        | 0.153           | 125.767              | +                  | 1.332         |

three tetrahedra bundles (Fig.3b, Fig.3d) tiled layers.

As what mentioned in electronic structure subsection i, the  $Q^{2-}$  contribute most to the transition from occupied states to unoccupied states. And compare with the zinc-blende structure whose  $Q^{2-}$  are  $sp^3$  hybridization and four coordinate to cations, the  $Q^{2-}$  ions are two coordinate and three coordinate in  $AX_2MQ_6$  and  $AX_4M_5Q_{12}$  respectively.

In  $AX_2MQ_6$ , the  $Q^{2-}$  is  $sp^3$  hybridization and two coordinate which lead to the appearance of two pairs of lone pairs in each Q atoms. The location of the lone pairs ought to be the bond of zinc-blende structure. However, replacement of atoms and structure distortion make the lone pairs deviate from the origin location.

We attribute the different birefringence to the acentricity of  $Q^{2-}$  i.e. the existent of lone pairs and their location deviation. Because  $Q^{2-}$  plays the decisive role in optical properties and displays remarkable anisotropy. Nevertheless, the location of lone pairs is hard to be quantification to reveal the quantitative relation between birefringence and structure. We therefore define a geometric feature the dihedral angle between tetrahedrons' underside and xy-plane. As show in Fig.3b and Fig.3d, the undersides of tetrahedrons have been labeled as  $\alpha$ ,  $\beta$  and  $\gamma$ , and the xy-plane was labeled as  $\Sigma$ . We defined the quantifiable dihedral angle to be  $\theta$ :

$$\theta = \frac{\angle(\alpha, \Sigma) + \angle(\beta, \Sigma) + \angle(\gamma, \Sigma)}{3} \quad (7)$$

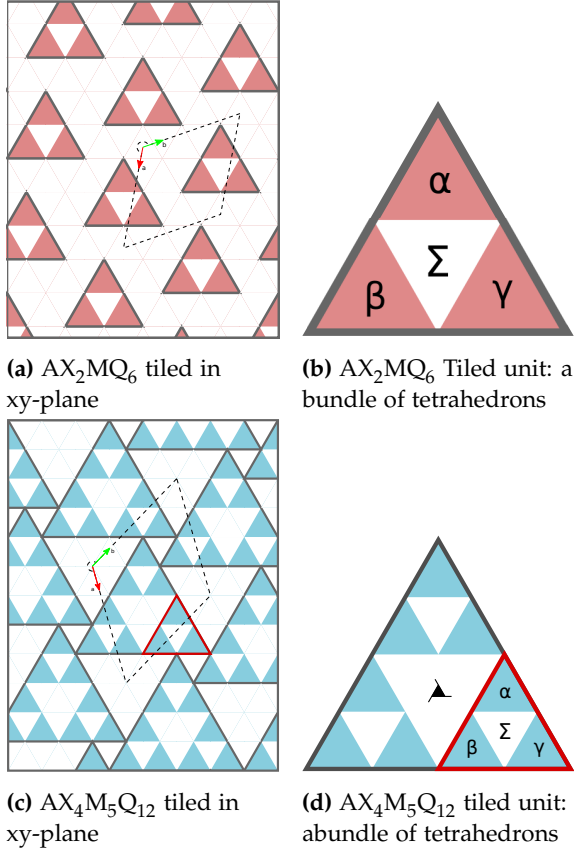
This geometirc feature can be measured easily by using structue viewer softwares such as VESTA<sup>33</sup> (as shown in Fig.4) after getting the crystal structure.

In  $AX_4M_5Q_{12}$ , the  $Q^{2-}$  have same hybridization but three coordinate which lead to the single lone pairs. The location of the lone pairs also deviated from the origin zinc-blende bond.

The birefringence of  $AX_4M_5Q_{12}$  crystals are extremely low  $<0.01$  in transmission frequencies. But the birefringence of  $AX_2MQ_6$  are variable in a wide range from 0.06(CsSi<sub>2</sub>GaS<sub>6</sub>) to 0.186(BaGa<sub>2</sub>SnSe<sub>6</sub>). The low birefringence of  $AX_4M_5Q_{12}$  is result partly from small radiu Cd atoms as we interperate from the relation of ion radius and birefringence.

However, the anisotropy of the crystal are contributed mostly from the acentricity of  $Q^{2-}$  which can be related to its lone paris positional deviation. As shown in Fig.3a and Fig.3c, the bundle of tetrahedrons are viewed from top to bottom along the c axis. We can find that for BaGa<sub>2</sub>SnSe<sub>6</sub> the lone pairs above the Q atoms are centralize to the  $C_{3v}$  axis while the small birefringence compounds CsGaSn<sub>2</sub>Se<sub>6</sub> and CsCd<sub>4</sub>Ga<sub>5</sub>Se<sub>12</sub> have the lone pairs locate at the direction where the original bonds locate of zinc-blende strucure. Using the parameter we definded to quantification the lone pairs' positional deviation, we find good correlation between birefringence and structure parameter as shown in Fig.5 which explains birefringen difference in all  $AX_2MQ_6$  and  $AX_4M_5Q_{12}$  struture.

Taking the biggest birefringence compound BaGa<sub>2</sub>Snse<sub>6</sub> as example, its large birefringence attribute to: 1. the large radius of Sn and Se atoms; 2. the strong acentricity i.e. lone pairs positional deviation which comes from the distortion between tetrahadrons. As mentioned before,  $AX_2MQ_6$  have more sparse network connection between tetrahedrons, therefore more freedom for atoms off-centeterd movement. However, the dense tetrahedral network of  $AX_4M_5Q_{12}$  makes atoms hard to deviate from central location and stay the isotropy as zinc-blende structure.



**Figure 3** Layers structure viewed from c-axis and its constructive units

## V. SUMMARY

Linear optical properties especially the anisotropy of R3 space group diamond-like framework crystal  $AX_2MQ_6$  and  $AX_4M_5Q_{12}$  was done with first-principles calculation.

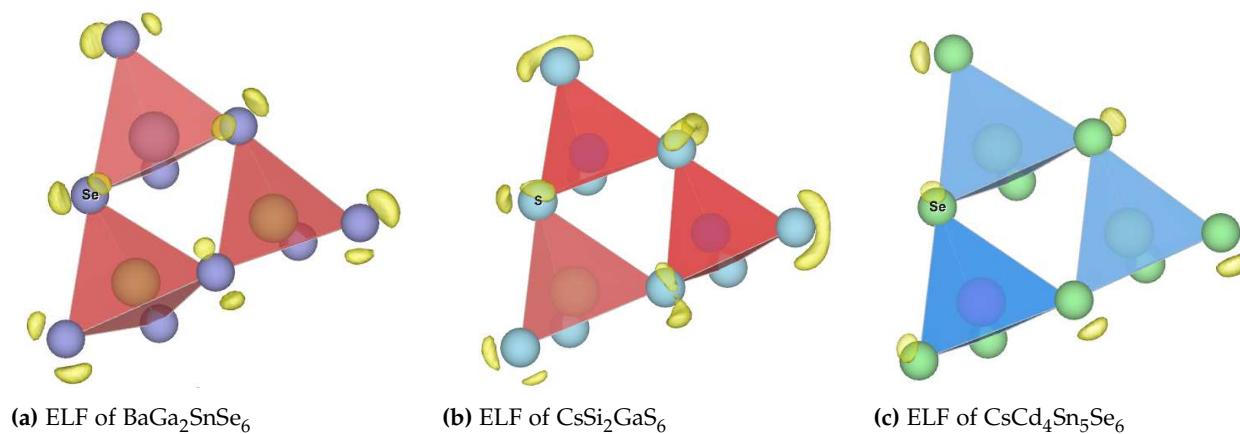
Both  $AX_2MQ_6$  and  $AX_4M_5Q_{12}$  are partial occupation compounds. The models of a reasonable configuration which can accurately reflect the material properties is hard to be chosen. We use SOD program to enumerate all possible configurations in a  $1 \times 1 \times 1$  hexagonal conventional cell and confirm that the  $P3_1$ (No.144) and  $P3_2$ (No.145) are reasonable configuration.

We also investigate the structural and electronic mechanisms of the anisotropic optical properties in these materials. On the one hand, we reveal the correlation of birefringence and framework ion radius that the birefringence is increase with bigger framework ion radius. On the other hand, geometric parameter the dihedral angles between xy-plane and tetrahedrons' underside was de-

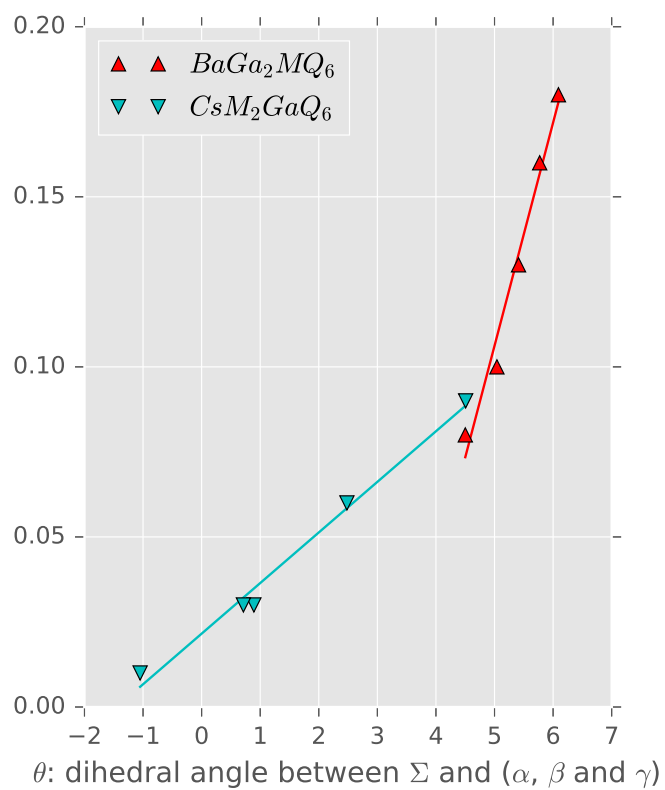
fined to quantificat the acentricity factor of anisotropy of crystal. The birefringence and dihedral angles between xy-plane and tetrahedrons' underside are well positive correlation. These two factors combined to explain the different birefringence of  $AXM_2Q_6$  and  $AX_4M_5Q_{12}$  from  $<0.001$  to  $0.186$ . And the phase matchability of these crystal can be explained with these birefringence data. For the existent of geometric-property relationship, it is possible to control the anisotropy of crystal by adjusting the geometric parameter.

Meanwhile, by comparing birefringence we find the hypothetical structures  $CsQ_2GaM_6$  ( $Q=Ge, Si$ ;  $M=Se, S$ ) are unlikely to reach phase matching condition. We believe that the evaluation of structure-property correlation in our work has implications in the exploration of new IR-NLO crystals with good performance.





**Figure 4** ELF of  $\text{BaGa}_2\text{SnSe}_6$ ,  $\text{CsSi}_2\text{GaS}_6$  and  $\text{CsCd}_4\text{Sn}_5\text{Se}_6$



**Figure 5** Dependence of birefringence on defined dihedral angle  $\theta$



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VI. SI

|                                     |             |            |           |
|-------------------------------------|-------------|------------|-----------|
| BaGa <sub>2</sub> SiS <sub>6</sub>  | a           | c          | V         |
| exp                                 | 9.5544(2)   | 8.6498(4)  | 683.82(2) |
| PBEsol                              | 9.462       | 8.556      | 663.318   |
| PBE                                 | 9.710       | 8.716      | 711.641   |
| pz-LDA                              | 9.355       | 8.484      | 643.081   |
| BaGa <sub>2</sub> SiSe <sub>6</sub> | a           | c          | V         |
| exp                                 | 9.967(1)    | 9.047(2)   | 778.3(2)  |
| PBEsol                              | 9.925       | 9.006      | 768.225   |
| PBE                                 | 10.188      | 9.210      | 827.810   |
| pz-LDA                              | 9.799       | 8.959      | 744.981   |
| BaGa <sub>2</sub> GeS <sub>6</sub>  | a           | c          | V         |
| exp                                 | 9.6020(1)   | 8.6889(2)  | 693.78(2) |
| PBEsol                              | 9.502       | 8.623      | 674.275   |
| PBE                                 | 9.740       | 8.840      | 726.317   |
| pz-LDA                              | 9.375       | 8.608      | 655.176   |
| BaGa <sub>2</sub> GeSe <sub>6</sub> | a           | c          | V         |
| exp                                 | 10.008(1)   | 9.090(2)   | 788.4(2)  |
| PBEsol                              | 9.949       | 9.093      | 779.410   |
| PBE                                 | 10.208      | 9.377      | 846.335   |
| pz-LDA                              | 9.803       | 9.097      | 757.133   |
| BaGa <sub>2</sub> SnSe <sub>6</sub> | a           | c          | V         |
| exp                                 | 10.1449(14) | 9.2490(18) | 824.4     |
| PBEsol                              | 10.054      | 9.326      | 816.477   |
| PBE                                 | 10.315      | 9.639      | 888.085   |
| pz-LDA                              | 9.908       | 9.334      | 793.519   |

**Table 4** Lattice parameters compare with experiment data

| Models                       |               |             |
|------------------------------|---------------|-------------|
| Crystal                      | Configuration | Energy (Ry) |
| $\text{BaGa}_2\text{SiS}_6$  | No.143        | -1750.217   |
|                              | No.144        | (-)0.020    |
|                              | No.145        | (-)0.044    |
| $\text{BaGa}_2\text{SiSe}_6$ | No.143        | -1836.936   |
|                              | No.144        | (-)0.020    |
|                              | No.145        | (-)0.036    |
| $\text{BaGa}_2\text{GeS}_6$  | No.143        | -2348.947   |
|                              | No.144        | (-)0.031    |
|                              | No.145        | (-)0.014    |
| $\text{BaGa}_2\text{GeSe}_6$ | No.143        | -2435.772   |
|                              | No.144        | (-)0.023    |
|                              | No.145        | (-)0.012    |
| $\text{BaGa}_2\text{SnSe}_6$ | No.143        | -2249.162   |
|                              | No.144        | (-)0.017    |
|                              | No.145        | (-)0.004    |

**Table 5** Ground state energy of different configurations